

THE EMISSION BAND SPECTRUM OF AsO

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Plate VII

ABSTRACT. The band spectrum of AsO excited in a heavy current discharge run on a 2000 volt, 1 ampere transformer, revealed a large number of new bands in the region λ 4100– λ 3400Å. They have been analysed into two systems. The lower state frequency for both these systems has been found to be equal to the ground state frequency of the molecule. The molecular constants found for these two systems are summarised below:

$$E-X^2\Pi_r: \nu_e = \frac{27095.5 \text{ cm}^{-1}}{26802.5 \text{ cm}^{-1}}; \omega_e' = 714 \text{ cm}^{-1}$$

$$x_e' \omega_e' = 2.5 \text{ cm}^{-1}; \omega_e'' = 963 \text{ cm}^{-1} \text{ and } x_e'' \omega_e'' = 4.5 \text{ cm}^{-1}$$

$$F-X^2\Pi_r: \omega_e'' \simeq 964 \text{ cm}^{-1}; \omega_e' \simeq 689 \text{ cm}^{-1}$$

INTRODUCTION

In an earlier publication on this molecule, Lakshman and Rao (1960) reported two new doublet band systems designated as $C^2\Delta-X^2\Pi_r$ and $D(^2\Pi^-)-X^2\Pi_r$ in the region λ 3100– λ 2400Å. Prior to this, Connelly (1934), Jenkins and Strait (1935), Shawhan and Morgan (1935), all about the same time reported independently two doublet systems $A^2\Sigma-X^2\Pi$ and $B^2\Sigma-X^2\Pi$ of AsO, in emission, in various sources of excitation in the region λ 3450– λ 2350Å. All these four systems reported namely, $A-X$, $B-X$, $C-X$, and $D-X$, have a common lower $^2\Pi_r$ state, with a doublet splitting of 1026 cm^{-1} . Connelly's absorption experiments proved this lower $^2\Pi$ system as the normal ground state of the AsO molecule.

The investigations on this molecule have been continued in order to obtain a band system analogous to the $A^2\Pi-X^2\Pi$ system, earlier found in SbO by Mukherji (1931), Sen Gupta (1939), Lakshman and Rao (1960), and Shimauchi (1960). This work has led to the analysis and identification of two new systems designated as $E-X^2\Pi$, and $F-X^2\Pi$, in the band spectrum of the AsO molecule. The present paper deals with a detailed analysis of the bands of this system.

EXPERIMENTAL

Experimental procedure adopted in the present investigations was the same as reported earlier by Lakshman and Rao (1960), except that a 2kv transformer had been used instead of a 4kv transformer. The bands are so very feeble in intensity, that exposures varying from 20 to 45 minutes were found necessary to photograph them on Ilford Special Rapid, Ilford Panchromatic and Agfa Isopan Superspecial plates using a Hilger Medium Quartz Spectrograph. Wavelengths of the band heads were made using iron arc lines as standards. The vacuum wave numbers were obtained from Kayser's tables.

RESULTS

New bands obtained in the region $\lambda 4100\text{--}\lambda 3400\text{\AA}$ are reproduced in plate VII. Though the bands are sharp they are so very feeble in intensity that all our attempts failed to photograph them with reasonable intensity on a large Littrow Spectrograph.

The new red degraded bands start from the long wave length side of the $A-X$ system, i.e. about $\lambda 3400\text{\AA}$ and extend upto nearly $\lambda 4100\text{\AA}$. It was at first thought that they could be the extension of the $A-X$ system. Our attempts to fit them into the vibrational scheme of the $A-X$ system were not successful. Therefore, it was concluded that they might fall into one or more separate systems. The wave length, wave number, intensity and classification of these band heads are all given in table I.

F-X $^2\Pi$ system :

Bands with heads at $\lambda 3628.8$, $\lambda 3659.8$, $\lambda 3690.5\text{\AA}$ appear to form one sequence with a wave number interval approximately equal to 235 cm^{-1} . Similarly another sequence of bands could be picked up with heads at $\lambda 3510.2$, $\lambda 3541.1$, and $\lambda 3570.9\text{\AA}$, giving almost the same wave number interval. Further a wave number interval equal to 931 cm^{-1} is found between the bands at $\lambda 3510.2$ and $\lambda 3628.8\text{\AA}$. This is close to the $\Delta G_{5/2}$ value of the lower $X\ ^2\Pi$ state of the AsO molecule. Taking this as a clue, the other bands as far as they could, have been picked up to fit into a vibrational scheme as shown in Table II.

The rest of the bands could very well be fitted into two components of a doublet system, with a doublet interval of 733 cm^{-1} in the upper state. Therefore it is quite propable to assume that the other component of this $F-X\ ^2\Pi$ system has not been excited in the mode of excitation adopted by the authors. The approximate vibrational constants of this system are given hereunder :

$$\omega'_0 \simeq 689\text{ cm}^{-1}; \omega''_0 \simeq 964\text{ cm}^{-1}$$

TABLE I

Wave length, Wave number, Intensity and Vibrational assignments of the bands of $E-X\ ^2\Pi$ and $F-X\ ^2\Pi$ systems

λ A	ν cm ⁻¹	Intensity Assignment	
E-X $^2\Pi_{3/2}$			
3521.8	28386	1	2,0
3551.4	28148	2	3,1
3611.4	27682	1	1,0
3706.3	26973	1	0,0
3740.6	26726	1	1, 1
3842.1	26020	4	0,1
3987.1	25074	1	0,2
E-X $^2\Pi_{3/2}$			
3650.5	27386	2	1,0
3682.3	27149	2	2,1
3747.1	26680	1	0,0
3920.8	25498	1	1,2
4032.7	24790	1	0,2
F-X $^2\Pi$			
3428.0	29163	2	(V'+2,2)
3479.0	28736	2	V', 1
3510.2	28480	5	V'+1, 2
3541.1	28232	3	V'+2, 3
3570.9	27996	4	V'+3,4
3596.9	27794	4	V', 2
3628.8	27549	4	V'+1, 3
3659.8	27316	3	V'+2, 4
3690.5	27089	2	V'+3, 5

TABLE II
Vibrational Scheme of the band heads of the $F-X^2\Pi$ system of AsO

$V' \backslash V''$	0	1	2	3	4	5
V'	28736	942	27794			
			686			
$V'+1$			28480	931	27549	
			683		683	
$V'+2$			29163	931	28232	916
					680	
$V'+3$					27996	907
						27089

$E-X^2\Pi$ system

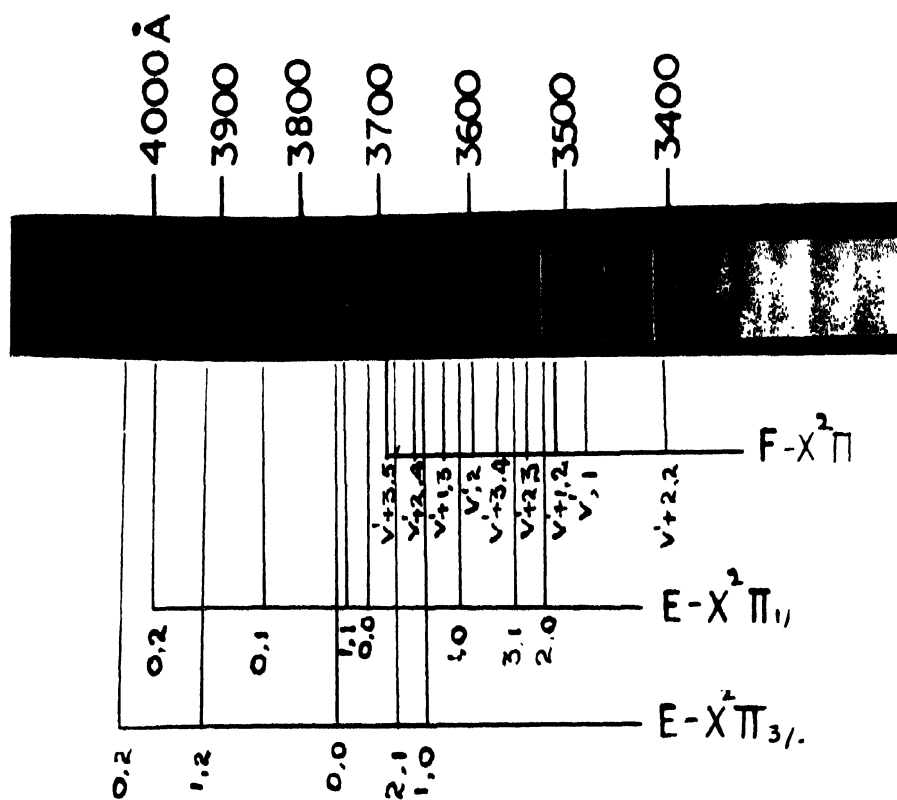
Table III gives the Deslandre's scheme for the two components of this system. The band heads of the two components of this system could be represented by the quantum formula :

$$\nu = \frac{27095.5}{26802.5} + 714(V' + \frac{1}{2}) - 2.5(V' + \frac{1}{2})^2 - 963(V'' + \frac{1}{2}) + 4.5(V'' + \frac{1}{2})^2$$

to within an accuracy of 3 cm^{-1} .

TABLE III
Vibrational scheme of the band heads of the $E-X^2\Pi$ system of AsO

$V' \backslash V''$	0	1	2
0	26973	953	26020
	26680	—	—
	709	—	—
	706	—	—
7	27682	956	26726
	27386	—	—
	704	—	—
	—	—	—
2	28386	—	—
	—	—	—
	—	27149	—
3	—	28148	—
	—	—	—



Medium Quartz Spectrogram
The new E-X & F-X Systems of AsO

DISCUSSION

The ground state electron configuration for the AsO molecule can be written in Mulliken's notation as

$$(Z\sigma)^2 (Y\sigma)^2 (x\sigma)^2 (\omega\Pi)^2 (V\Pi) \dots {}^2\Pi,$$

A study of the ionised spectra of molecules gives us a clue to know which of the two bonding orbitals ($x\sigma$) or ($\omega\Pi$) is possessing higher energy than the other. As Π state has been observed as the first excited state in the case of NO^+ and NS^+ we may expect for molecules with small internuclear distance $\omega\Pi$ orbital to lie inside the $x\sigma$ orbital. As ${}^1\Sigma$ state has been observed as the first excited state in the case of PO^+ , PS^+ and AsO^+ , we may expect for molecules with large internuclear distance $x\sigma$ orbital to lie inside the $\omega\Pi$ orbital.

The states E and F may then be expected to belong to the following configuration.

$$(Z\sigma)^2 (Y\sigma)^2 (x\sigma)^2 (\omega\Pi)^3 (V\Pi)^2 \dots 2\Pi_i, {}^2\Pi_r, {}^2\Pi, {}^4\Pi_i$$

The $E-X$ system may belong to a $E^2\Pi_r-X^2\Pi_i$ transition with a splitting of 733 cm^{-1} in the upper E state. Similarly the $F-X$ system may belong to a $F^2\Pi-X^2\Pi_i$ transition with upper ${}^2\Pi$ state belonging to Hund's case (b). The nature of the states can however be only confirmed on the basis of a detailed rotational analysis.

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